California Regional PM_{10} and $PM_{2.5}$ Air Quality Study (CRPAQS)

Statement of Work – CRPAQS Data Analysis Task 6.3
Evaluation of Secondary PM Transport

STI-902332-2300-WP
Sonoma Technology, Inc.

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Introduction

In this task, STI will characterize the relative roles of transport and diffusion on the dispersion of particulate matter (PM) generated from various emission sources. The following questions will be addressed:

Task Question 1: What is the relative influence of transport, diffusion, and emission source location in explaining the regional nature of secondary ammonium nitrate and sulfate under low wind-speed/stagnant conditions?

Task Question 2: When and how do aloft NO_x emissions from industrial source get entrained into the shallow mixed layer?

Task Question 3: How do primary particles generated in urban areas arrive in non-urban areas and in other downwind urban areas under low wind-speed/stagnant conditions?

Technical Approach

STI will conduct a series of analyses using CALMET model wind fields, trajectories, and mixing heights created by STI in Task 5.2; CALPUFF dispersion modeling results and chemical mass balance (CMB) results to be completed by Desert Research Institute (DRI) in Task 4.1; analysis of other chemistry data at selected receptor sites; and analysis of emissions data. Our general approach is to use the meteorological data to determine if and how primary and secondary compounds are transported and dispersed under stagnant surface conditions and then review the air quality and emissions information to determine whether the air quality characteristics are consistent with the meteorological results.

For the purpose of this task, diffusion is defined as the mixing of material by turbulent and molecular processes; the term transport is defined as the advection of material, including advection of material in different directions at different levels due to sheared flows. Dispersion includes both diffusion and transport.

Task Question 1

We hypothesize that the regional nature of secondary ammonium nitrate and sulfate are due to a combination of meteorology and spatially dispersed ammonia emissions. Kumar et. al. (1998) showed that the San Joaquin Valley (SJV) is ammonia-rich, even in urban areas. Recent work in Salt Lake City, Utah, has shown that ammonia emissions from automobiles exist in sufficient quantity to support the formation of ammonium nitrate in urban areas (Coe et. al., 2000). Complicating matters in the SJV, feed lots that produce ammonia emissions are reasonably dispersed throughout the valley compared to NO_x emissions, which are predominantly along major roadways, in urban residential areas, and near the major industrial point sources; and SO_2 emissions are confined to point sources and are extremely small. Less dispersion of ammonia, compared to NO_x and SO_2, is required to support ammonium nitrate and ammonium sulfate formation throughout the SJV. To explain the regional nature of secondary ammonium nitrate and sulfate, we will focus primarily on the meteorological mechanism(s) that may account for the dispersion of NO_x and SO_2 while accounting for the influence of the spatial variability of ammonia, NO_x, and SO_2 emissions.

The formation of nitric acid (which rapidly converts to ammonium nitrate under cool, moist conditions) takes from four to six hours (at a 3% to 5% per hour consumption rate of NO_x), and the lifetime of this secondary aerosol is a few days in the absence of significant fog. This means that the meteorological processes that disperse the NO_x and nitrate need to occur on a time scale of one-half day and a space scale of a few hundred kilometers to account for the regional nature of ammonium nitrate. Even under light wind conditions, we suspect that diffusion alone is not strong enough to account for the dispersion required for this time and space scale. Therefore, we hypothesize that the regional nature of ammonium nitrate and sulfate is mainly a result of transport of air parcels, which may vary in direction and magnitude by altitude, especially during overnight hours when several stratified layers within the planetary boundary layer (PBL) can exist. These air parcels, which exist at different altitudes and can follow different pathways at night, can mix together during the day as the mixing layer height increases due to surface heating. This process disperses the NO_x, ammonium nitrate, SO_2 and ammonium sulfate. Because the formation of sulfate depends greatly on the chemical production pathway and because sulfate is a small fraction of the total PM mass, we will focus on nitrate formation to define the time and space scales for the meteorological analyses.

Given the above information, we will address the regional nature of secondary ammonium nitrates and sulfates under low-wind-speed/stagnant conditions by performing the following tasks:

- Review ammonia, NO_x, and SO_2 emissions data and confirm the regional or sub-regional nature of these emissions (based on spatial variability).
- Use wind field, trajectory, and diffusion results from Task 5.2 to evaluate the amount of dispersion on stagnant stable winter episode days at various levels within the PBL. To do this we will interpret the results from Task 5.2 and complete dispersion estimates using CALMET and CALPUFF.
- Create spatial plots of dispersion as indicated by tracers released in the model from various urban sources for selected episode days. We will then use the mixing height

analyses from Task 5.2, and perform additional mixing height analyses if needed, to determine the relationships among transport at various altitudes, mixing, and the dispersion of urban material throughout the SJV.

- Validate the dispersion results by comparing the air quality data (secondary ammonium nitrate and sulfate observations) monitored at rural and urban sites to the dispersion estimates.

Task Question 2

During the measurement phase of CRPAQS, there were no parameters measured that would allow differentiation of elevated point source NO_x emissions from mobile source NO_x emissions. Therefore, to determine if and how aloft NO_x emissions from industrial sources get entrained into the shallow mixed layer, we will rely only on emissions, meteorological, and model data. In particular, we will

- Obtain NO_x emissions data from major elevated point sources in central California. We will then calculate the effective stack heights at various times of day for these point sources for up to 10 selected days.
- Calculate forward trajectories using the CALMET wind fields from Task 5.2 and obtain ARB's MM5-based trajectories to determine when these stack emissions might impact sites in the SJV.
- Use the mixing height data estimated in Task 5.2 to determine when these aloft emissions can mix into the shallow surface layer.
- Use the CALPUFF model and the CALMET wind fields from Task 5.2 to perform three-dimensional dispersion model runs from the selected point sources.
- Compare the CALPUFF results to the trajectory and mixing height results to check the consistency between the methods.

Task Question 3

We will evaluate the extent to which primary particles generated in urban areas arrive in both non-urban and other urban areas under low-wind-speed/stagnant conditions by reviewing meteorological data, potential transport paths, CMB results, and observed air quality data at the rural sites. The meteorological data will include profiler winds, CALMET model wind fields, trajectories, and mixing heights. The observed air quality data will include elemental carbon (EC, also called black carbon), NO, and NO_y data. EC is a good indicator of urban motor vehicle emissions and, to a lesser extent, wood-smoke emissions. The ratio of NO to NO_y is a good indicator of the age of the air parcel, where an NO/NO_y ratio close to 1 indicates very fresh emissions, and an NO/NO_y ratio close to zero indicates aged emissions. If the emissions are aged and there are significant levels of EC, the primary particles are most likely from an upwind urban area and not from local sources. If the emissions are fresh with significant levels of EC, the primary particles may be from local sources. Organic carbon data will also be considered as an urban tracer; however, we recognize that there are non-urban sources associated with this chemical and it may be difficult to use.

We will use CMB results from Task 4.1 to support the results from the analysis of the EC and NO/NO_y. CMB analyses from the 1988–1989 San Joaquin Valley Air Quality Study (Chow et al., 1992) showed that multiple source types could be identified. These source types include dirt, motor vehicles, vegetative burning, tire and brake wear, crude oil, marine air, construction, and secondary organics. Assuming that similar source types will be identifiable from the CRPAQS data, motor vehicles, tire and brake wear, and construction are probably the best candidates for identifying urban sources. Vegetative burning is a fair candidate to identify burning of wood in fireplaces and woodstoves; however, agricultural burning would also be grouped into this category, and it is not associated with urban sources. Cooking emissions will likely not be separately identifiable since cholesterol data were not collected. We assume that CMB analysis will be performed at all stations with elemental data (from the XRF), which will include rural anchor sites such as Angiola, Bethal Island, and Sierra Nevada, and several other rural satellite sites.

Using the above information, we will evaluate the extent to which primary particles generated in urban areas arrive in non-urban and urban areas under low-wind-speed/stagnant conditions by performing the following tasks:

Calculate forward-trajectories and back-trajectories from urban sites and back-trajectories from selected rural sites where EC and NO/NO_y data and/or CMB information exists. The trajectories will be calculated using the CALMET wind fields from Task 5.2 at multiple altitudes within the PBL for up to 10 selected episode days. We will use this information to determine whether there is transport from urban to urban areas and from urban to rural areas on these days.

- Determine if and when air parcels at different levels can mix to the surface along these trajectory paths by reviewing the mixing height data estimated in Task 5.2.
- Review the CMB results and the EC and NO/NO_y data collected at rural areas on selected episode days to estimate how much primary pollutant is transported from urban to rural areas.
- Compare the results from the meteorological analysis, EC and NO/NO_y analyses, and CMB analysis to determine whether the results from all these analyses are consistent. We will also identify potential causes of inconsistent results.

Task Staffing and Management

STI's overall project manger is Lyle Chinkin. The STI task manager assigned to this task is Mr. Clinton MacDonald. Dr. Paul Roberts will serve as a technical advisor for the data analysis, and Mr. Neil Wheeler will serve as a technical advisor for the modeling effort.

Schedule of Deliverables

Table 1 lists the deliverables to be prepared for Task 6.3 and their estimated delivery dates. The schedule for this task is somewhat dependent on the availability of results from other tasks. Additional time (and, potentially, resources) may be required if the products of other tasks are not received as planned .

Table 1. Estimated schedule of deliverables.

Deliverable	Deliverable Due Date
Submit final work plan	January 6, 2003
Perform modeling and analyses	July 2003
Prepare draft technical memorandum	August 2003
Submit final technical memorandum	September 2003
Submit peer-reviewed paper and conference presentation	October 2003

ARB Staff Assigned to this Task

The ARB Project Manager assigned to this Task is

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Data Products to Be Performed/Delivered by ARB

ARB will supply STI with back-trajectories of specified episodes. STI will work with ARB to determine how the data will be transferred to STI and in what format(s) the data will be provided.

Software and Models to be used by STI

STI will use the following software to complete work under this task:

- Microsoft Word
- Microsoft Excel
- Microsoft Access
- ArcGIS 8.2
- CALMET
- CALPUFF

References

Chow J.C., Watson J.G., Lowenthal D.H., Solomon P.A., Magliano K., Ziman S., and Richards L.W. (1992) PM10 source apportionment in California's San Joaquin Valley. Atmos. Environ. 26A, 3335-3354.

Coe D.L., Chinkin L.R., Ryan P.A., and Garver P. (2000) Conceptual model of important sources of particulate matter in the Salt Lake City region. Scoping Study prepared for the State of Utah Department of Environmental Quality, Salt Lake City, UT by Sonoma Technology, Inc., Petaluma, CA, STI-900031-1965-DSS2, April.

Kumar N., Lurmann F.W., Pandis S., and Ansari A. (1998) Analysis of atmospheric chemistry during 1995 integrated monitoring study. Report prepared for the San Joaquin Valleywide Air Pollution Study Agency, c/o the California Air Resources Board, Sacramento, CA by Sonoma Technology, Inc., Petaluma, CA, STI-997214-1791-FR, July.